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VI.—*On Portable Chemical Apparatus for Quantitative Mineral Analysis.*

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COMMUNICATED BY J. H. COLLINS.

TOWARDS the end of the last century one Professor Götting, who taught chemistry in the schools of Jena, conceived the idea of preparing a portable chest of chemistry, or complete collection of Chemical Tests.* Chemical knowledge being in those days somewhat limited, we are not surprised to find that the contents of the chest could be stowed within a space nine inches square by twelve deep.

This cosmopolitan collection was intended for the use of chemists, physicians, mineralogists, scientific artists, manufacturers, farmers, and the cultivators of natural philosophy. The tests were prepared by a Mr. Hunneman, a friend of the author, and pupil of Klaproth and Hermbstaedt of Berlin; and were put up in thirty five glass bottles and some small wooden boxes.

The tests, such as they are, are in general of a reliable nature, and in accordance with the state of chemistry at that time; but neither chemists,

* A copy of the small treatise which accompanied the collection, and which formerly belonged to Faraday, is now in the Library of the Chemical Society. The English version was published in 1791 in London, and was sold by Messrs. C. and G. Kearsleys, No. 46 Fleet Street, who also supplied the chests.

farmers, nor natural philosophers would derive much practical benefit from their application in this present generation.

The cabinet which I shall presently describe is principally intended for the use of mineralogical chemists, or persons who, having some knowledge of analytical chemistry, are familiar with the appearances presented by the crystalline and non-geometric but distinctive forms, which most common minerals possess. Those minerals also which occur in amorphous masses, in which it is impossible to detect a determinate crystalline shape, but which are technically of the greatest importance, can likewise be usually discriminated by their colour, lustre, hardness, density, &c. It is proposed, if possible, to supply minute directions with the cabinet, by the use of which careful persons, other than these, may arrive at reliable results.

In Professor Götting's little book, there is no attempt at anything beyond qualitative description. To find out whether a piece of mineral was iron or copper ore, whether a liquid was acid or alkaline, whether a rock was fusible or infusible—these and similar questions are all that it attempted to decide. In fact at that time the attention of scientific men was more bent upon qualitative than quantitative inquiry. To know of what substances the earth is made* occupied their minds more than the question, 'In what proportions are these substances allied to each other?' The discovery that a certain kind of rock contained copper, and that another kind of rock contained lead, were facts of greater significance to them than to us. The merchant and manufacturer now pay little or no attention to such results as these; the information they desire to obtain is of a quantitative character. The percentage of the valuable constituent and the quantity of the deleterious constituent or constituents are the items upon which they calculate. For example, the merchant now guarantees under penalty of forfeit that a cargo of Hematite shall contain at least (say) 55 p.c. of iron and not more than 0.10 p.c. of phosphoric acid, inasmuch as he knows that all iron ores contain iron and phosphoric acid, a qualitative examination is useless to him. Commercial transactions have been based upon the accurate determination to 0.01 p.c. of iron in a given sample: this it is acknowledged is drawing the line far too fine, but the tendency to scientific exactitude prevalent of late years marks a new era in Commercial Technology.

* Cronstedt's Mineralogy, which appeared in English in 1770, was the first systematic work in this field. He does not give any quantitative relations: neither does he mention in the attached description of a pocket laboratory, any attempt at quantitative estimations. Gustavus von Engestrom and Bergman wrote descriptive treatises upon pocket laboratories soon after Cronstedt's; but the discrimination of different substances occupied their sole attention.

Notwithstanding the repeated attempts made since Cronstedt's time to produce chemical cabinets which should be of value to the scientific traveller, Plattner was the first to work out* (1853) the means by which a miniature Laboratory of this nature could be rendered capable of performing accurate quantitative determinations. The patience and minute care which he bestowed upon the subject are too well known by members of this society to need mention here. He placed in the hands of chemists and mineralogists a portable cabinet which enabled them to determine the amount of silver, mercury, copper, tin, and iron present in minerals containing them. Of the processes described in his book that for the estimations of silver was capable of giving the most accurate results, and remains a monument of his skilful handicraft. We can however estimate copper and iron with much more accuracy than his processes permit of, by means of Volumetric Analysis. There are only two or three minerals of commercial importance of which the valuation made according to Plattner would avail commercially.† We must not forget however that Plattner's cabinet is mainly a metallurgical one, and that the estimations stand comparison better with metallurgical than with chemical assays: nearly all the determinations are done by the blowpipe, and wet methods are only introduced in a few instances. Ores of iron and zinc, of lead and manganese, cannot be valued by means of the blowpipe.

I have not yet been able to find any account of a portable chemical cabinet of appliances specially designed for, and shown to be able to perform the valuation of those common metals which are technically of the first importance. Nor am I aware that such a cabinet can be obtained in this country, or indeed abroad. My friend Mr. Collins tells me that he has felt the want of a cabinet which is neither a toy collection nor a set of lecture table apparatus. A few months since, being in expectation of making a visit to Servia, I worked at the processes about to be given with an idea of constructing a cabinet useful for the purposes of mining research.

Under what circumstances does the analytical chemist travelling abroad upon a mineral survey, pursue his vocation? He is usually away from the

* The previous work of Berzelius (1820) and of Harkort (1827) contributed, however, to Plattner's success.

† I do not wish in any way to undervalue the excellent work that is done all over the world by means of the blowpipe. A pocket case is of great service in the field, and enables the mineralogist to discriminate between valuable and non-valuable minerals in a number of instances: that is to say, between those which are worth and those which are not worth more accurate chemical investigation. While acknowledging the importance of Blowpipe Chemistry, I cannot acknowledge that it fulfils the requirements of technology in an adequate manner. Plattner's complete cabinet of Blowpipe apparatus sold in this country at 30 guineas, does not suffice for the scientific valuation of ores of the common metals.

vicinity of towns,—never, however far from some small village. Here he sojourns while making incursions into the surrounding country. After collecting his specimens he returns to the village and takes the first opportunity of making some determinations. Distilled water is not to be obtained unless the village apothecary has a still, and can be induced to use it; our chemist cannot burden himself by taking a sufficient supply. Kettles among non-tea-drinking people in the south of Europe are very rare; and should he succeed in obtaining one and concocting a condenser, his work would still be considerably delayed. Therefore he must be content to use the common water of the place, which if it gave a considerable precipitate with ammonia oxalate it might be advisable to boil and filter. By the system I adopt, however, common water may be used without purification. Provided that the water is fairly free from iron and suspended matter, a condition generally fulfilled, it may be used in the estimation of the constituents enumerated in the subjoined scheme of analysis. I have found a difficulty with the sulphur estimation: until that is satisfactorily overcome our chemist must wait for the wet season.

Another difficulty in out of the way places is to provide the source from which heat is derived. Gas is of course out of the question. In Italy and Spain there may sometimes be found among the culinary arrangements of the household, small round charcoal furnaces built in brick which are useful to heat an iron plate. But as a rule no casual sources of heat such as this should be relied upon. Oil can easily be obtained in the south of Europe, and need not form an item of the collection. It is burnt in an Argand lamp placed underneath an iron plate six inches in diameter. This serves to heat flasks and beakers, to boil water, and to evaporate liquids contained in small Berlin dishes, which are supported on the plate by tinned iron rings. A spirit lamp is used to ignite crucibles, &c. A flask of spirit is carried in the case, and the flask can be replenished in towns. Another Argand lamp heats a small air bath, the top-plate of which can be used for precipitation and slow evaporations. A Plattner's Blowpipe lamp is fed with equal volumes of oil and alcohol. Pisani recommends a mixture of six volumes of spirits of wine and one of oil of turpentine, to which is added several drops of ether. He found that this liquid gave a bright flame, and evolved no unpleasant odour, its heating power when urged by the blowpipe was sufficient to fuse the end of a platinum wire 0.2 mm. in diameter, and to melt an iron wire of 0.3 mm. in diameter into a globule of a millimetre in radius. He was also able to melt 23 grams of silver, and to cupel 5 grams. of argentiferous lead by its means.

We now come to consider the nature of the processes employed. The principle upon which they are worked out lies in the employment of $\frac{1}{10}$ th

of the quantity of substance usually operated upon, and both re-agents and appliances are similarly arranged in miniature. The centner of 100 mg. was first I believe used by Plattner, and this is the quantity of mineral which is used in the estimations. Gravimetric determinations are avoided where practicable, and volumetric processes supply their place. The greatest objection to such a course of procedure is that the eye is not as delicate in discriminating end reactions as the operator might wish. My own power of discriminating tints is rather below than above the average. I think I may state however, that determinations of the common metals may be made without the error exceeding 1 p.c. of the substance operated upon. I think I may go further;—if 100 milligrams of mineral be taken—such minerals for example as calamine, hematite, copper pyrites, carbonate of lead, chromic iron,—the variation from the truth which careful determinations will exhibit will not exceed 0.5 mg. and will be frequently considerably closer.

The estimations which are of most importance in the valuation of minerals for commercial purposes may be given as follows:—

1. Iron ores—iron, phosphoric acid, silicious residue.
2. Manganiferous iron ores—manganese in addition to the above.
3. Chrome iron ores—chromium.
4. Manganese ores—manganese peroxide and manganese.
5. Copper ores—copper.
6. Lead ores—lead and silver.
7. Zinc ores—zinc.
8. Cassiterite—tin, iron, silicious matter.
9. Cobalt ore—cobalt protoxide.
10. Antimony ore—antimony.
11. Mineral phosphates—phosphate of lime ($\text{Ca}_3 \text{P}_2 \text{O}_8$).

(1.) IRON ORES.

The iron is measured volumetrically by bichromate of potassium. The standard solution is made so that 1 c.c. shall equal 4 mg. of iron. As the bichromate can be obtained nearly pure in the shops, by taking the theoretical quantity, the right standard is very nearly obtained. Theoretically 1.758 grams. should be dissolved in half a litre of water; the solution then oxidizing 4.000 mg. of iron per c.c. As a mean of two results 1.756 gram. was required in practice; another sample of bichromate gave 1.754 gram. The purity of the salt however must not be relied upon, and in this case as in every other the true value of the standard liquid must be found by direct titration.

The spotting is done with a very dilute solution of potassium ferricyanide, a drop of which should give but a faint tinge of yellow when

placed on the porcelain plate. The acid solution of iron-chloride after complete reduction by zinc, is carefully and rapidly turned into a small Berlin dish, and titrated. It should not measure more than 20—30 c.c. including the washings of the flask. When the end reaction appears on the plate a little ferricyanide is run into the dish by means of a fine piece of glass tube, the same in fact with which the spotting on the plate is done. A green coloration denotes that a drop or two more bichromate is required; a whitish or yellowish coloration shows when the reaction point is reached.

With the burettes used one drop is sufficient to produce the final change in a definite and recognizable manner. The drops let fall by the burettes weigh about 27 mg. and correspond to 1.1 decimilligram of iron or 0.11 p.c. upon a centner of 100 mg. of iron ore. The burette used is an ordinary 20 c.c. Mohr. and its readings are correct to within 0.02 cubic centimetre.

Each cubic centimetre is divided into 10 parts, and each part is again divided into 10 by the eye, this can be done after a little practice with ease and accuracy. One hundredth of a cubic centimetre is thus read off, and as there are 37 drops of 27 mg. each in 1 c.c., a fraction of a drop may be measured. This is, however, usually unnecessary. Under these circumstances the following results were obtained with fine-drawn soft iron wire; the wire contains 99.8% of iron, a constant by which the weight of iron taken is multiplied.

1 c.c. Bichromate = 4.000 mg. iron.

<i>Iron wire taken.</i>	<i>Equal to Pure Iron.</i>	<i>c.c. of $K_2 Cr_2 O_7$.</i>	<i>Iron found.</i>
A 70.0 mg.	63.9 mg.	17.54 c.c.	70.16 mg.
B 79.0 "	78.8 "	19.71 "	78.84 "
C 61.8 "	61.7 "	15.40 "	61.60 "
*D 49.64 "	49.64 "	12.41 "	49.64 "

A sample of micaceous iron ore was next operated upon. My friend Mr. W. E. Dawson determined the iron in this ore in the ordinary manner, and found it to amount to 62.33 p.c. I may state that as a rule my results are slightly higher than his owing, to a slight difference made in judging the final reaction. Five centners (or 500 mg.) of the dried ore were dissolved in hydrochloric acid, the liquid was diluted and filtered into a 50 c.c. measuring flask.

A. 10 c.c. (= 100 mg. taken) took 15.64 c.c. $K_2 Cr_2 O_7$ = 62.56 p.c.

B. 10 " " " 15.65 " " = 62.60 p.c.

* 5 c.c. of a standard sol. of $FeSO_4$ were taken, 50 c.c. of which solution was known to contain 0.4964 gm. iron as $FeSO_4$.

The solution of ferric chloride is reduced with pure re-distilled zinc. This can be obtained in Germany at about 6 marks a kilo. The reduction is conducted in a small flask on an iron plate, the flask being covered with a watch glass; or a test tube may be used.

Phosphoric Acid.—This estimation can be effected with accuracy by weighing the phospho-molybdate precipitate obtained from 5 centners of ore. The errors when the operation is conducted in accordance with the principles observed by persons of experience does not exceed 0.01 p.c. The precipitation is conducted at a temperature of from 50°—60°C; the whole bulk of liquid not exceeding 30c. c. Five centners of ore containing 0.05 p.c. of phosphoric acid gives a precipitate weighing 7.5 mg. which can be weighed to a fraction. Boussingault's constant of 0.0373 is used to deduce the phosphoric acid; 0.01 p.c. P_2O_5 should be added for loss and solubility. The yellow precipitate, it should be mentioned, is washed off the filter into a small platinum dish in which it is dried on the iron plate and afterwards weighed.

Silicious Residue.—This determination is made gravimetrically in the ordinary manner upon 500 to 1000 mg. of ore, the filtrate from which is used for the other estimations. The results agree to within 0.2—0.3 p.c. The silica in the residue can be determined by fusion. The silicious residue should be determined *after evaporation to dryness*, and so stated.

If it is important to notice if an ore is calcareous or silicious in nature, a rough indication may be obtained by observing if the addition of an acid produces a strong evolution of carbonic acid.

(2.) MANGANESE PEROXIDE.

This is estimated in Pyrolusite, &c., by boiling about 200 mg. of the ore weighed in a small glass tube in acidulated ferrous sulphate solution; 1000 mg. of cryst. ferrous sulphate is dissolved in a hot boiled 10 p.c. sulphuric acid solution in a flask, the tube containing the manganese is carefully dropt in after decomposition, the liquid is titrated with bichromate. Ferrous sulphate is taken to contain $\frac{1}{3}$ of its weight of iron; I find it to be more exact than taking the theoretical figure. A blank assay was made without putting the manganese into the flask, the liquid being boiled for a $\frac{1}{2}$ hour by itself. It yielded the following results: iron taken 44.44 mg., iron found 44.44 mg.

Manganese.

Metallic manganese is estimated with accuracy by Pattinson's method (Q. J. Chem. Soc. June 1879, p. 365), upon 100 mg. of ore. Every particular has to be conducted upon the miniature scale adopted in this system of analysis. The ore is dissolved in a flask with a few cubic

centimetres of hydrochloric acid, and about 100 mg. of anhydrous ferric chloride is added after the excess of acid has evaporated, and 10 or 15 c.c. of water has been added. The liquid is now neutralized with chalk, until a slight precipitate falls, ten c.c. of a clear solution of bleaching powder are now added and 50–60 c.c. of boiling water; the liquid is immediately neutralised with 250 mg. of chalk and well stirred; it should be placed on the hot iron plate for a few minutes but not boiled. The flocculent precipitate is brought upon a filter and washed until the washings are shown to be free from chlorine by a drop of potassium iodide and starch. The filtrate must be pink; 0.10 p.c. of manganese is added for the manganese converted into permanganate, which is lost. While this is going on, 600 mg. of ferrous sulphate crystals are accurately weighed, and dissolved in 50 c.c. of hot 10 p.c. (vol.) solution of sulphuric acid. The filter with its contents is placed in a small dish, the ferrous sulphate is poured upon it, and, after stirring, the liquid is titrated with bichromate. The constant from Fe found to Mn wanted is 0.431. In manganiferous iron ores ferric chloride is not wanted. A manganese ore gave

Manganese present 47.39 p.c. Manganese found 46.73 p.c.

(3.) COPPER.

De Haen's method is used, but the iodine solution is dispensed with. The copper is separated from the ore as sulphide by boiling the sulphuric acid solution with sodic hyposulphite. The sulphide is roasted in a porcelain crucible, and treated with hydrochloric and a few drops of nitric acid. After evaporation it is treated with sodic acetate and one gram. of potassium iodide, and the copper estimated with hyposulphite and starch. The hyposulphite solution is made so that 1 c.c. = 1.0 mg. of copper, but this standard will decrease,* and must be tested every few weeks with pure copper.

A standard solution was made from a stronger solution, the titre of which was known. A standard solution of pure copper was made, 5 c.c. of which contained 25.25 mg. of copper :

1 c.c. hyp. = 1.000 mg. copper.

<i>Copper taken.</i>	<i>c.c. taken.</i>	<i>Copper found.</i>
25.25 mg.	25.1 c.c.	25.1 mg.
25.25 "	25.3 "	25.3 "
25.25 "	25.25 "	25.25 "
25.25 "	25.5 "	25.5 "
25.25 "	25.5 "	25.5 "
Mean 25.25	25.33 c.c.	25.33 mg.

Ammonium carbonate (1 grm.) is added to preserve this solution.

I think I may therefore assert that the copper estimation can be made within 0.5 p.c. of the truth. For the whole of the copper present in the ore is completely separated by hyposulphite of sodium sulphuric acid solution, and the substances which may possibly contaminate the precipitate do not interfere with the reactions. If the analysis of very rich ores is contemplated, the hyposulphite solution should be twice as strong.

(4.) SILVER.

Silver is estimated metallurgically according to the directions of Plattner, the blowpipe apparatus commonly used is therefore included in the cabinet.

(5.) LEAD.

There is a volumetric method for the estimation of lead by precipitation as chromate, and the subsequent titration of the chromic acid set free by sulphuric acid from the isolated salt. This method can be applied to all lead minerals, is rapid, and yields fairly accurate results. Carbonates of lead are dissolved in nitric acid, sodic acetate is added and then potassium bichromate; the lead chromate deposits at a gentle heat and can be filtered and washed with rapidity with galena; where the nitric acid produces sulphate of lead, the bases in the solution are converted into sulphates, and the sulphate of lead, &c., is filtered as usual. This latter is converted into carbonate of lead by digestion with carbonate of soda, the precipitate is filtered off, dissolved in acetic acid, and treated with potassium chromate.

In operating with small quantities I have found that sulphuric acid does not set free the whole of the chromic acid. Small quantities of undecomposed chromate may be seen by the eye. The following experiments establish this fact; 50.0 mg. of pure lead was precipitated from its acetic acid solution as chromate. The chromate of lead after filtration was placed in a dish together with its filter, and an excess of ferrous sulphate together with dilute sulphuric acid was added to it. The whole was boiled for some minutes, but traces of chromate of lead were still visible. It was then titrated by bichromate (4.000 mg.) of which it took 2.52 c.c. (=10.08 mg. Fe). The ferrous sulphate taken corresponded to 49.6 mg. iron. Therefore $49.6 - 10.08 = 39.52$ mg. iron, which, multiplied by the constant for deducing lead from iron: gives— $39.52 \times 1.232 = 48.7$ mg. of lead found, instead of 50.0 mg. taken. Another experiment gave 47.2 mg. instead of 50.0 mg. In order to obviate these important errors, another course was finally adopted. The amount of chromic acid in solution after the lead had precipitated was determined. To the acetic acid solution of lead 14.95 c.c. of bichromate

solution was added; the liquid was warmed and filtered. To this filtrate 49.6 mg. of iron, in the form of ferrous salt was added. The excess of ferrous salt took 7.53 c.c. of bichromate.

$$14.95 \times 7.53 \text{ c.c.} = 22.48 \text{ c.c. } K_2 Cr_2 O_7 \times 4.000 = 89.92 \text{ mg. iron}$$

$$\text{Iron in ferrous salt used} = 49.60 \text{ ,, ,,}$$

$$\text{Chromic acid withdrawn by lead} = 40.32 \text{ ,, ,,}$$

To deduce lead: $40.32 \times 1.232 = 49.67$ mg. lead found, instead of 50.0 mg. of lead taken.

Four burette readings of bichromate were taken in this experiment, and the error of the estimation was 0.33 mg. lead. This corresponds to 0.07 c.c. of the burette. The error of a reading need not amount to more than 0.02 c.c., and therefore since these errors would not extend always in the same direction, the burette measurements need not introduce any serious source of error.

(6.) ZINC.

If sulphide of zinc could be washed without loss, this metal might be advantageously determined by ferric chloride and bichromate. But the foregoing is a difficulty which renders the process useless to the practical assayer. The best results I obtained exhibited considerable deviation from the amounts of zinc taken, owing to this source of error, for example:—

<i>Zinc taken.</i>	<i>Bichromate taken.</i>	<i>Zinc found.</i>
20.0 mg.	9.03 c.c.	21.0 mg.

Schaffner's process was found to be impracticable with small quantities of substance; the same may be said of the ferricyanide and iodine method. Fairly good results were obtained with potassium ferrocyanide in hydrochloric acid solution, using uranium as indicator; and I consider this method to be reliable, and more applicable to the estimation of small quantities of zinc than any other with which I am acquainted.

Potassium ferrocyanide like potassium bichromate can be obtained in England tolerably pure; a weighed quantity will therefore give a standard approaching the true one. The theoretical equivalent however must not be taken, because the composition of the precipitate formed is not established. To make a solution 1 cubic centimetre of which shall equal 2.00 mg. of zinc, 4.4 grams. of ferrocyanide should be dissolved in 500 c.c. of water. Two separate samples of the salt were used to make two standard solutions, each equal to 2.00 mg. of zinc per cubic centimetre; in the one case 4.33 grams. ferrocyanide were required, and in the other 4.42 grams.

The operator finds the standard of his solution by means of pure zinc, a stock of which he carries with him. The zinc is separated from the

iron in the ore, &c., by double precipitation with ammonia. Manganese in quantity interferes with the accuracy of the results, but is not often present in calamine and blende. Copper if present is separated from the sulphuric acid solution by boiling with a gram. of sodium hyposulphite; after oxidizing any iron present, the liquid is precipitated by carbonate of soda, and evaporated somewhat in a porcelain dish, the precipitate is re-dissolved in a little hydrochloric acid after filtration, and the iron is separated by ammonia as usual. The bulk of the liquid before titration should not exceed 20—30 c.c.

The following results have been obtained:—

I. The standard solution was equal to 1.50 mg. zinc per c.c. known weights of pure zinc were taken.

<i>Zinc taken.</i>	<i>c.c. taken.</i>	<i>Zinc found.</i>
33.2 mg.	22.0 c.c.	33.0 mg.
34.6 „	23.0 „	34.5 „
34.6 „	23.0 „	34.5 „
34.6 „	23.6 „	35.4 „

The last result was produced in the presence of 5 c.c. concentrated hydrochloric acid, showing that considerable excess of acid must be avoided.

<i>Zinc taken</i>	<i>c.c. taken</i>	<i>Zinc found</i>
25.0 mg.	16.8 c.c.	25.2 mg.
32.4 „	21.9 „	32.5 „

II. Another standard solution of zinc (1 c.c. = 2.58 mg.) was made. The following determination was made in acidulated ammonium chloride solution, to correspond with the actual testing.

<i>Zinc taken</i>	<i>c.c. taken</i>	<i>Zinc found</i>
40.0 mg.	15.5 c.c.	40.0 mg.

In an acid solution containing no ammonium chloride two determinations gave.

<i>Zinc taken</i>	<i>c.c. taken</i>	<i>Zinc found</i>
40.0 mg.	15.7 c.c.	40.5 mg.
20.0 mg.	7.8 c.c.	20.1 mg.

The standard of the ferrocyanide should be determined in the presence of 0.5 to 1.0 gram. of ammonium chloride. In these experiments the reactions were distinguishable to within 0.2 c.c. Care *must* be taken that the ferrocyanide is run in a few c.c. at a time, with shaking. The testing must be continued until the addition of 0.2 c.c. from the last reaction produces, upon standing for a moment or so, a permanent deepening in the colour of the spot.

Zinc can be estimated in the manner described to within 1 p.c. of the true content of the ore. A correction of 0.5 p.c. might perhaps be added in the case of ores containing much iron or copper.

I have made a few estimations by this process in some complex metallic sulphides containing Blende from Sardinia, and obtained the following results.

<i>Gravimetric determinations.</i>		<i>Miniature Volumetric.</i>	<i>Difference.</i>
		<i>Method.</i>	
Zinc	24.54%	24.63%	0.09%
Zinc	11.54 „	11.86 „	0.32 „
Zinc	18.01 „	18.38 „	0.37 „

(7) TIN.

Cassiterite is assayed by boiling 1 grm. of the mineral with strong hydrochloric acid to remove iron; in rich ores about 0.1 p.c. of tin oxide is rendered soluble by this operation. The insoluble residue is dried and fused under crude potassium cyanide in a small crucible. About a gram. of ore should be taken, the principal source of error lies in uncertainty as to whether the whole of the tin has collected in the button: of two assays therefore the highest should be taken.

(8) COBALT.

Cobalt is estimated by boiling the mineral containing it with aqua-regia in a small conical flask: after evaporating the excess of acid the liquid is neutralized with sodium carbonate, and a hot concentrated solution of potassic acetate is added to precipitate the iron, arsenic acid, silica, &c. The filtrate is evaporated to 10 or 15 c.c. and 3 c.c. of a saturated solution of potassic nitrite rendered acid by acetic acid, is added. The cobalt nitrite is dried and weighed as usual. Two centners of ore are taken for the estimation.

(9) ANTIMONY.

One centner is boiled with aqua-regia; tartaric acid, ammonia and ammonium sulphide are added, and the liquid is filtered. Acetic acid precipitates arsenic and antimony in the filtrate. These are separated by Bunsen's method, using sodium sulphite acidulated with hydrochloric acid. The antimony is weighed as Sb_2O_4 .

(10) PHOSPHATE OF LIME.

This estimation is made by uranium solution of which 1 c.c. = 2.00 mg. phosphoric acid.

To prepare the liquid to be titrated the following procedure is adopted. The sample is powdered, and ground in the agate mortar until soft to the

touch, *like flour*. Five centners are weighed, placed in a clean dish and mixed with cold 5 p.c. solution (volume) of dilute sulphuric acid, by triturating with a pestle; 20 c.c. of this acid suffices. The last few cubic centimetres are used to wash out the dish after the contents have been poured into a 50 c.c. flask; a little water may also be used. After standing for several hours, with occasional shaking the liquid is made up to the mark and 0.3 c.c. water added. The whole is filtered through a dry filter into a dry flask. Ten cubic centimetres (= 100 mg.) are neutralized with carbonate of soda and made just acid with acetic acid; the titration is then proceeded with. Another 10 c.c. should be used to check the result. Some crystals of pure uneffloresced rhombic phosphate of soda are contained in the cabinet and are used to standardize the uranium solution. Of this salt 1.01 gram. is weighed off (after powdering and pressing between filter paper), dissolved in water and made up to 100 c.c. 10 c.c. of this liquid (= 20.0 mg. P_2O_5) is placed in a flask, a few drops of carbonate of soda and finally of acetic acid are added (to acid reaction), and the liquid is titrated hot as usual.

A phosphate containing 35.86 p.c. of phosphoric acid was found to contain 35.99 p.c. P_2O_5 when working with a uranium solution 1 c.c. of which equalled 1.290 mg. P_2O_5 .

Having described the analytical methods adopted, we now come to consider the arrangements by means of which they are carried out.

For this purpose it will be convenient to consider these arrangements under four heads, namely;—

1. The measuring apparatus and standard solutions.
2. General apparatus for analytical work.
3. Chemicals, liquid and solid.
4. Cabinet arrangement.

1. *The measuring apparatus, &c.*

The balance is constructed with the special object of portability. It takes a maximum weight of 10 grams and indicates accurately 0.0001 grams.—(one deci-milligram). A folding glass case is erected over it when in use and packs into the same box, occupying a space of about $8 \times 8 \times 3$ inches.

The burettes, two in number, are of Mohr's construction. They measure 20 c.c. of liquid, with a delicacy of measurement of within

1 c.c. They are supported by a brass upright 10 inches long which screws into the centre of a rectangular base. This base, or foot is half covered with a porcelain plate which is screwed into it. This serves for spot reactions. These burettes, their stand and appurtenances, are fitted exactly in a box 8 inches wide 15 inches long and 2 inches in external thickness. This box contains moreover six pipettes, one 10 c.c., one 5 c.c., two 2 c.c., and two 1 c.c. in capacity; the whole arrangement is independent, so to speak, of the rest of the cabinet.

Four standard solutions are carried in the case. Each bottle contains 500 c.c. of liquid, which seems to me to be the minimum quantity consistent with the objects in view. Potassium Bichromate, Potassium Ferrocyanide, Uranium Acetate, and Sodid Hyposulphite are found to be sufficient for most practical purposes. These bottles have well ground stoppers which are tied down by caoutchouc caps. Two more 500 c.c. bottles containing ammonia and hydrochloric acid are fastened down in like manner. The six bottles are contained in a drawer $10\frac{1}{2} \times 15 \times 8$ inches, in which the burette box likewise finds a place.

Four measuring flasks are provided, of respectively, 250, 200, 100 and 50 c.c. capacity. They are contained in a drawer of the same case.

2. *Apparatus.*

1. Plattner's blowpipe apparatus for cupellation; in separate case.
2. Platinum crucible and dish; platinum wire, and swing for crucibles; platinum forceps.
3. Six porcelain crucibles; six porcelain dishes for evaporation, (smallest size). One three inch porcelain dish for iron tests. Tinned ring supports.
4. Copper drying bath (hot air) with holes in top for basins, crucibles, &c.
5. Round iron plate (6-in). Iron wire gauze 1 sq. ft.
6. Heating apparatus. Two small argand burners for oil; a ring support slides on the brass upright. One spirit lamp: a tin can containing $\frac{1}{2}$ litre of spirit.
7. Beakers, 2 sets of three (small size). Flasks of 60-70 c.c. capacity, eight.
8. Funnels, assorted, six: close and open filter paper 12 packets.
9. Miscellaneous: test tubes, watch glasses, stirring rods &c.
10. Two washing bottles of 250 c.c. capacity, for hot and cold water.

3. *Chemicals (liquid and solid.)*

1. Six 250 c.c. glass bottles containing nitric, sulphuric, and acetic acids; ammonium sulphide, ammonia nitro-molybdate, and carbonate of soda, (solutions.)

2. Sixteen two ounce re-agent bottles containing ferrous sulphate, carbonate of soda, carbonate of lime, anhydrous ferric chloride, sodic phosphate, potassium dichromate, potassium ferrocyanide, potassium chlorate, sodic sulphite, potassic cyanide, bleaching powder, barium chloride, potassium nitrite, sodic acetate, potassium iodide and potassium ferrieyanide.

3. In small turned wood boxes: starch, pure lead, electro-type copper, and litmus paper.

4. A bag of redistilled zinc, free from iron.

4. *Cabinet Arrangement.*

The aforesaid re-agents and appliances are contained in two cases of hard wood for the sake of portability. A strong leather handle is affixed to the top of each case so that it may be carried like an ordinary portmanteau. The cases are of the same size, viz. 13-in. deep, 17-in. high, and 17-in. in diameter (the depth is given at right angles to the height when the case is standing upright). The first case contains simply two drawers with partitions in which the burette box, the standard solutions, the flasks, and miscellaneous glass apparatus find their place.

The second case contains one drawer, the rest being open spaces, in which are stowed the balance, the blowpipe apparatus, the liquid and solid reagents, the heating apparatus and miscellanea. By these arrangements the cases are weighted as evenly as possible. Both cases are bound in green baize or leather and studded with brass nails.

N.B. The chests will be made by Messrs. E. Cetti & Co., of Holborn, the celebrated glass apparatus manufacturers.